

Chemistry 312

Supplementary Notes on the First Law of Thermodynamics

Work. The general concept of work is familiar from elementary mechanics. In thermodynamics work is defined as a quantity that flows across the boundary of a system during a change in state and which can be completely converted into the raising or lowering of a weight in the surroundings. Work is an algebraic quantity, taken to be positive by definition when it flows from the surroundings to the system. One never talks about work inside a system. Work is produced in the surroundings because of an unbalance of forces across a boundary. No transfer of matter is involved.

Kinds of work: In principle, all kinds of work are completely convertible into each other. Because of its importance in thermodynamics, we will focus special attention on the work produced by varying the volume of a system (so-called "expansion work" or "compression work"), which we will denote by W_C :

$$W_C = -P_{\text{ext}} dV; W_C = - \int_{V_1}^{V_2} P_{\text{ext}} dV \quad (1)$$

where P_{ext} is the applied pressure on the system and V is the volume of the system. P_{ext} is measured in the surroundings. It may or may not be equal to the pressure of the system. The integral (and therefore W_C) will depend on the path between state 1 (with volume V_1) and state 2 (volume V_2). If the expansion process is carried out reversibly P_{ext} will be equal to P , the pressure of the system at each point along the path.

All other kinds of work will be called external work and may be denoted by W_X . A few examples include the work performed on the system by varying the:

(a) height (h) of a system of mass m in a gravitational field with local acceleration g :

$$W = -m g dh$$

(b) velocity (v) of a system of mass m : $W = -mv dv$

(c) length (L) of a rod by applying a force f : $W = -f dL$

(d) area (A) of a surface film with a surface tension :

$$W = - \gamma dA$$

(e) charge Q (not to be confused with the heat) of a capacitor with a potential difference V (not to be confused with the volume!) across its plates: $W = -V dQ$

Properties of work. It is an experimental fact that the total work does not sum to zero for most processes that start and end in the same state (cyclical processes). I.e., in general $\oint W \neq 0$. The consequences of this are:

(1) A system in a specified state does not contain a definite fixed amount of work.

(2) W is not a function of a set of independent state variables, such as $W(P,T)$ for a pure substance in a single aggregation state.

(3) W is not an exact differential but simply an infinitesimal amount of work.

Temperature and Thermal Equilibrium: Zeroth Law

It is a fundamental empirical fact that a property called "temperature" can be assigned to every equilibrium state of a system. Our primitive knowledge of temperature comes from human nerve sensations (ice and boiling water feel different), but there are also several different physical properties of systems which change with temperature (volume of a liquid, resistivity of a metal, etc.). The ability to define a scale to establish numerical values of the temperature depends on the concept of thermal equilibrium and the so-called "zeroth" law of thermodynamics.

Consider two systems enclosed by rigid boundaries that prohibit the passage of matter and chemical, electrical or mechanical energy, etc. If these are placed in "thermal contact" with each other and isolated from the surroundings, the properties of both will, in general, change with time. After a while these changes will cease, and the systems are then said to have come to thermal equilibrium. It is found that, if system B is in thermal equilibrium both with systems A and C, then A is in thermal equilibrium with C. This universal property (sometimes called the "zeroth law of thermodynamics") permits the concept of a temperature and suggests ways

of establishing empirical temperature scales by using the temperature dependent properties of some standard test object.

How to proceed in practice in defining a temperature scale depends on the choice of: the standard system (e.g., the length of a column of mercury), the fixed points for calibration (e.g., 0° for ice and 100° for steam), and an interpolation scheme for points other than the fixed points (e.g., taking t to be linear in the length of the mercury column). These choices are essentially arbitrary, and different choices will lead to different temperature scales.

Heat: The process of attaining thermal equilibrium is described as a "flow of heat" from the "hot" object to the "cold" one. Heat is a quantity that flows across the boundary of the system during a change in state by virtue of a difference in temperature between the system and its surroundings. Heat is an algebraic quantity, taken to be positive when it flows from the surrounds to the system (same convention as for work). Thermodynamic heat is always measured in the surroundings, not in the system. A quantity of heat (Q) may be established, for example, by the amount of temperature increase it causes if transferred to a fixed amount of water (the "calorie" is defined as the amount of heat required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C at a pressure of 1 atm).

Properties of heat. As in the case of work, we find experimentally that the total heat flow for a cyclical process does not sum to zero: $\oint Q \neq 0$. The consequences of this for Q are the same as those given above for W . The question of how to define the positive direction of work or heat is arbitrary. In modern thermodynamics, the usual convention is that heat is positive when absorbed by the system. Recall that work was similarly defined to be positive when work is done on the system by the surroundings. (In older texts, the convention for work is often the opposite of this, so be careful).

First Law of Thermodynamics.

When a system undergoes any cyclical process, the work given up from the surroundings is proportional to the heat withdrawn from the surroundings. The constant of proportionality (a negative number for the

sign conventions we have adopted) depends only on the units in which heat and work are measured. The Joule experiment permits one to relate units of work (joule) with units of heat (calorie). The relationship is now established by defining the calorie in terms of the more fundamental unit, the joule. One calorie is defined as 4.1640 joule (exactly).

When the same units are used for W and Q:

$$\circ W + \circ Q = 0 \text{ for } \underline{\text{all}} \text{ cycles.} \quad (2)$$

Definition of energy. In thermodynamics the energy U (sometimes called the internal energy) is defined by

$$dU = Q + W. \quad (3)$$

Thus for every cyclic process:

$$\circ U = 0 \quad (4)$$

Equations (3) and (4) together constitute a complete mathematical statement of the first law.

Properties of the energy. The consequences of Eq. (4) are:

- (1) U is a state variable (a single-valued extensive property of the system) and is completely defined except for an additive constant;
- (2) For unit mass of a pure substance in a single aggregation state, $U = U(V,T)$ and dU is the total differential of U(V,T);
- (3) dU is an exact differential;
- (4) The increase in energy U for any change in state is independent of the path, and depends only on the initial and final states:

$$U = U_2 - U_1 = \int_1^2 (Q + W). \quad (5)$$

Note that Q and W do depend on the path, but $Q+W (= \Delta U)$ does not. The symbol ΔU will be used only for state variables such as U. ΔU represents the change in the energy content between state 2 and state 1, while Q or W represents the amount of heat or work which flows across the system's boundaries for a given process which takes the system along a specified path from state 1 to state 2.